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Exergy valorization of a water electrolyzer and CO₂ hydrogenation tandem system for hydrogen and methane production

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In this work, we introduce a water electrolysis and CO₂ hydrogenation tandem system which focuses on methane generation. The concept consists of a water electrolyzer thermally coupled to a CO₂ hydrogenation reactor, where the power required to generate hydrogen comes from renewable energy. A thermodynamic analysis of the tandem system was carried out. Our analysis exposes that it is possible to increase the exergy efficiency of the water electrolyzer and CO₂ hydrogenation system by thermal coupling, where the thermal energy required to split water into H₂ and O₂ during the electrolysis process is compensated by the heat generated during the CO₂ hydrogenation reaction. Here, the conditions at which high exergy efficiency can be achieved were identified.

According to measurements done by the greenhouse gases observing satellite (GOSAT), the concentration of CH₄ and CO₂ in earth's atmosphere has been increasing continuously in the recent years¹. This indicates that the exploitation of fossil fuels to generate the energy required to meet our modern needs is not only threatening a shortage in our limited fuel sources but also damaging our environment. In order to decarbonize our energy supply, alternative energy technologies must be considered^{2,3}. The use of hydrogen as energy carrier is a promising way to encourage the decarbonization of energy, since it can be produced from the splitting process of H₂O (water electrolysis), which generates H₂ and O₂ without exhausting carbon to the environment as long as the energy required to achieve this process comes from renewable sources^{4,5}. The hydrogen obtained from the electrolysis process can be used to hydrogenate a CO₂ source where CH₄ and H₂O are produced, this process is known as Power-to-Gas (PtG)^{6–10}. PtG is a technology that connects the electrical power grid with the gas lines by converting excess electricity into a gas that can be injected to the existing gas distribution pipelines.

The PtG process is similar to life support systems for closed environments like the one that is currently used at the International Space Station (ISS), where O₂ and H₂O are the desired products to support life^{11,12}. O₂ and H₂ are obtained from water electrolysis. H₂ is used to convert the metabolic CO₂ generated by the ISS crew to produce H₂O which generates CH₄ as a byproduct. The obtained H₂O can be used to generate O₂ while the obtained CH₄ is vented to outer space.

Power-to-Gas technology is a promising alternative to recycle a global CO₂ and reduce carbon emissions to our atmosphere, especially when the energy required to generate H₂ comes from renewable sources like photovoltaic systems and wind turbines^{5,7,10}. Since the supply of energy coming from renewable sources is not constant, it fluctuates depending on demand and weather conditions, a H₂ generation system able to operate intermittently has to be adopted. A Polymer electrolyte membrane (PEM) water electrolysis system is a good option to meet the required intermittent operation. These systems are more operational flexible comparing to alkaline and solid oxide electrolysis cell systems^{13–15}.

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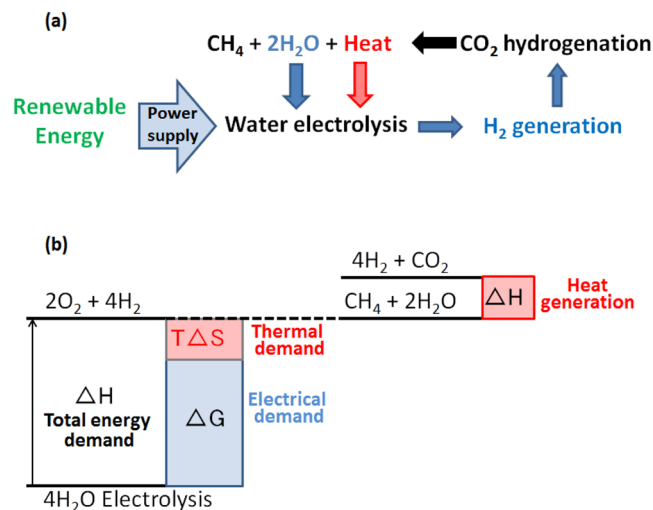


Figure 1. Schematic illustration of the Power-to-Gas concept. **(a)** The system consists of supplying renewable energy to power a water electrolyzer to generate H_2 , then this H_2 is used to hydrogenate CO_2 and produce CH_4 (this process is known as the Sabatier reaction). **(b)** Thermodynamic concept: the theoretical energy required to split liquid H_2O into gaseous H_2 and O_2 is equal to the enthalpy change (ΔH_{elec}) of H_2O , which is the sum of the Gibbs free energy change (ΔG , electrical demand) and entropy change times the temperature ($T\Delta S$, thermal demand). By exchanging the heat generated by the Sabatier reaction to compensate the water electrolysis thermal demand $T\Delta S$, the overall efficiency of the system can be improved.

PEM water electrolysis in combination with a CO_2 hydrogenation reactor is an attractive way for converting electric power coming from renewable sources into CH_4 . Other alternative to generate CH_4 from renewable energy is the co-electrolysis of H_2O and CO_2 in solid oxide cells (SOECs)^{16,17}. However, these cells are operated at very high temperatures, which make their design and operation more complicated than PEM electrolysis cells.

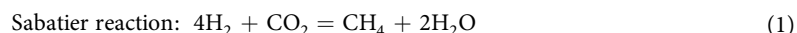
The hydrogenation process to convert CO_2 into CH_4 , also known as the Sabatier reaction, is a highly exothermic process which generates a lot of heat^{18–20}. This heat has to be removed from the Sabatier reactor in order to maintain a relatively low temperature. Avoiding high operation temperatures of the Sabatier reactor helps to prevent catalyst sintering which decreases the catalyst lifetime^{12,18–21}.

The efficiency of a water electrolyzer–Sabatier reactor system can be improved by thermally coupling the system. To split water into H_2 and O_2 , the electrolyzer demands electrical and thermal energy. The removed heat from the Sabatier reactor can be supplied to the electrolyzer, which will reduce the thermal energy demand and then the overall efficiency of the system is improved. A schematic illustration of the system concept is shown in Fig. 1a. This PtG system consists of supplying renewable energy to power a water electrolyzer to generate H_2 , and then this H_2 is used to hydrogenate CO_2 and produce CH_4 . The efficiency of the system can be increased by exchanging the heat generated during the hydrogenation process of CO_2 to the water electrolysis process. The thermodynamic concept of the system is shown in Fig. 1b. The theoretical energy required to split liquid H_2O into gaseous H_2 and O_2 is equal to the enthalpy change (ΔH_{elec}) of H_2O , which is the sum of the Gibbs free energy change (ΔG , electrical demand) and entropy change times temperature ($T\Delta S$, thermal demand). By exchanging the heat generated by the Sabatier reaction to compensate the water electrolysis thermal demand $T\Delta S$, the overall efficiency of the system can be improved. However, it is necessary to identify the conditions at which a maximum efficiency can be achieved. For this, an exergy analysis of the system is required to identify optimal operating conditions. Exergy valorization analysis is a useful technique to quantify the maximum work potential of a system. This thermodynamic analysis is also used to identify the factors or parameters that affect the efficiency of a process^{22–24}.

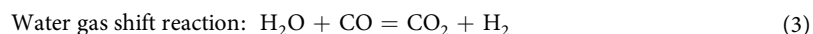
In this work, an exergy analysis of a water electrolyzer and CO_2 hydrogenation tandem system is presented. Operating conditions at which high exergy efficiency can be achieved are identified.

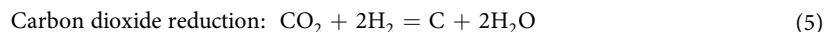
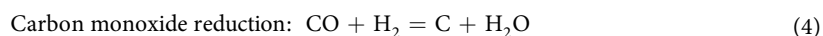
Results and Discussion

Thermodynamic analysis of CO_2 hydrogenation process. The equilibrium composition of the CO_2 hydrogenation process was computed following the Gibbs energy minimization method, see Methods for more details. The main reaction to convert CO_2 into methane is the Sabatier reaction:



Also during the CO_2 hydrogenation process the following side reactions can take place:





To analyze the influence of temperature, pressure and feed H_2/CO_2 molar ratio on the CO_2 hydrogenation products, equilibrium compositions were obtained at different conditions. Figure 2a shows the equilibrium composition of the CO_2 hydrogenation process at $\text{H}_2/\text{CO}_2 = 4$, 0.1 MPa and different temperatures. It is observed that the largest mole fraction of CH_4 and H_2O products are obtained at low temperatures (100–300 °C), indicating that the Sabatier reaction is favored at low temperatures, where a high conversion of CO_2 into CH_4 can be achieved. At high temperatures, CH_4 generation decreases and CO appears which means that the water gas shift reaction is favored. Figure 2b shows the thermodynamic conversion of CO_2 at 0.1, 0.5 and 1.0 MPa, $\text{H}_2/\text{CO}_2 = 4$ and different temperatures. A high conversion is observed at low temperatures, it is also noticed that a high conversion can be maintained at higher temperatures by increasing the pressure. The effect of H_2/CO_2 molar ratio on the CO_2 hydrogenation products and CO_2 conversion is shown in Fig. 2c,d. Under these conditions, the CO_2 conversion decreases with temperature and the generation of solid carbon (C) is favored. The presence of solid carbon affects the performance of catalyst, since the catalyst can be deactivated when solid carbon is deposited on it. To prevent the deactivation of catalysts, it is important to identify the conditions at which solid carbon can be generated. Figure 2e shows the carbon generation at 4 and 2 H_2/CO_2 molar ratios, and at different temperatures and pressures. It is observed that when the H_2/CO_2 molar ratio of 4 is not maintained, solid carbon is generated, while at a temperature above 590 °C this carbon generation is not observed under any conditions. This temperature coincides with the operating temperature of the Sabatier reactor used on the International Space Station¹¹, probably as a measure to prevent the generation of carbon when the H_2/CO_2 ratio of 4 cannot be maintained.

Exergy analysis of the Sabatier process. The exergy efficiency of the Sabatier process is defined by

$$\eta_{\text{Sabatier}}^{\text{ex}} = \frac{\text{CH}_{4,\text{out}} \cdot (\text{Ex}_{\text{CH}_4})}{\text{H}_{2,\text{in}} \cdot (\text{Ex}_{\text{H}_2})} \quad (6)$$

where $\eta_{\text{Sabatier}}^{\text{ex}}$ is the Sabatier exergy efficiency, Ex_{CH_4} and Ex_{H_2} are the exergy of CH_4 and H_2 , respectively. Details of the exergy calculations are described in the methods section. Figure 3 shows the exergy efficiency of the Sabatier process for H_2/CO_2 molar ratio of 4 (a) and 2 (b) at 0.1, 0.5 and 1.0 MPa as a function of temperature. In the case of the H_2/CO_2 molar ratio of 4 (Fig. 3a), the highest efficiency is observed in the temperature range of 100–150 °C and starts decreasing with temperature. In the case of the H_2/CO_2 molar ratio of 2 (Fig. 3b), the highest efficiency is observed at 340 °C for 0.1 MPa, while for 0.5 and 1.0 MPa it is observed at 400 °C and 420 °C, respectively. The exergy efficiency of the Sabatier process is proportional to the CH_4 generation flow rate, and this rate has a high dependency on temperature and H_2/CO_2 molar ratio as can be observed in Fig. 2a,c.

Exergy analysis of the system. The overall exergy efficiency of the system is defined by the following equation:

$$\eta_{\text{overall}}^{\text{ex}} = \frac{\text{Ex}_{\text{out}}}{\text{Ex}_{\text{in}}} \quad (7)$$

where $\eta_{\text{overall}}^{\text{ex}}$ is the overall exergy efficiency, Ex_{out} is the exergy output and Ex_{in} is the exergy input. Here, Ex_{out} is equal to $\text{CH}_{4,\text{out}} \cdot (\text{Ex}_{\text{CH}_4})$, while Ex_{in} corresponds to the electrical energy required to generate hydrogen from water electrolysis, more details on the calculations are given in the methods section. Figure 4 shows the overall exergy efficiency of the system for H_2/CO_2 molar ratio of 4 (a) and 2 (b) as a function of Sabatier temperature. In the case of the H_2/CO_2 molar ratio of 4 (Fig. 4a), the overall exergy efficiency has a maximum at 200 °C. While in the case of the H_2/CO_2 molar ratio of 2 (Fig. 4b), the maximum is found at 340 °C. The maximum overall exergy efficiency is achieved when the thermal exchange between the water electrolyzer and CO_2 hydrogenation reactor reaches its optimal point. This indicates that the thermal coupling within the system increases the exergy efficiency.

Our exergy valorization analysis identifies the three main parameters that contribute to achieve high exergy efficiencies for the water electrolyzer – CO_2 hydrogenation system. The first parameter is the H_2/CO_2 feed gas molar ratio. When this molar ratio is lower than 4, the methane generation rate decreases and solid carbon is generated, Fig. 2c,e. The second parameter is the Sabatier reaction temperature. CH_4 generation is favored in the temperature range of 100–300 °C, while at higher temperatures the water gas shift reaction takes, affecting the CH_4 generation, Fig. 2a. The third parameter that contributes to the enhancement of the system is the thermal coupling of the water electrolyzer and Sabatier reactor. The heat generated by the Sabatier reaction compensates the water electrolysis thermal demand ($T\Delta S$), which contributes to increase the overall exergy efficiency of the system, Fig. 4a. In the case of co-electrolysis of CO_2 in H_2O , it has been shown that this system is also able to achieve high exergy efficiencies to generate H_2 and CH_4 . However, the water gas shift reaction has a significant effect on the system efficiency^{16,17}. As mentioned above, this reaction is favored at high temperatures and this type of CO_2 co-electrolysis is carried out at high temperatures. In order to mitigate the effect of the water gas shift reaction and increase the efficiency of the system, CH_4 has to be fed through the cell anode.

Since the focus of the present work is the exergy valorization of the water electrolysis- CO_2 hydrogenation tandem system, a detailed cost analysis is not included. However, a few remarks can be made on the operating

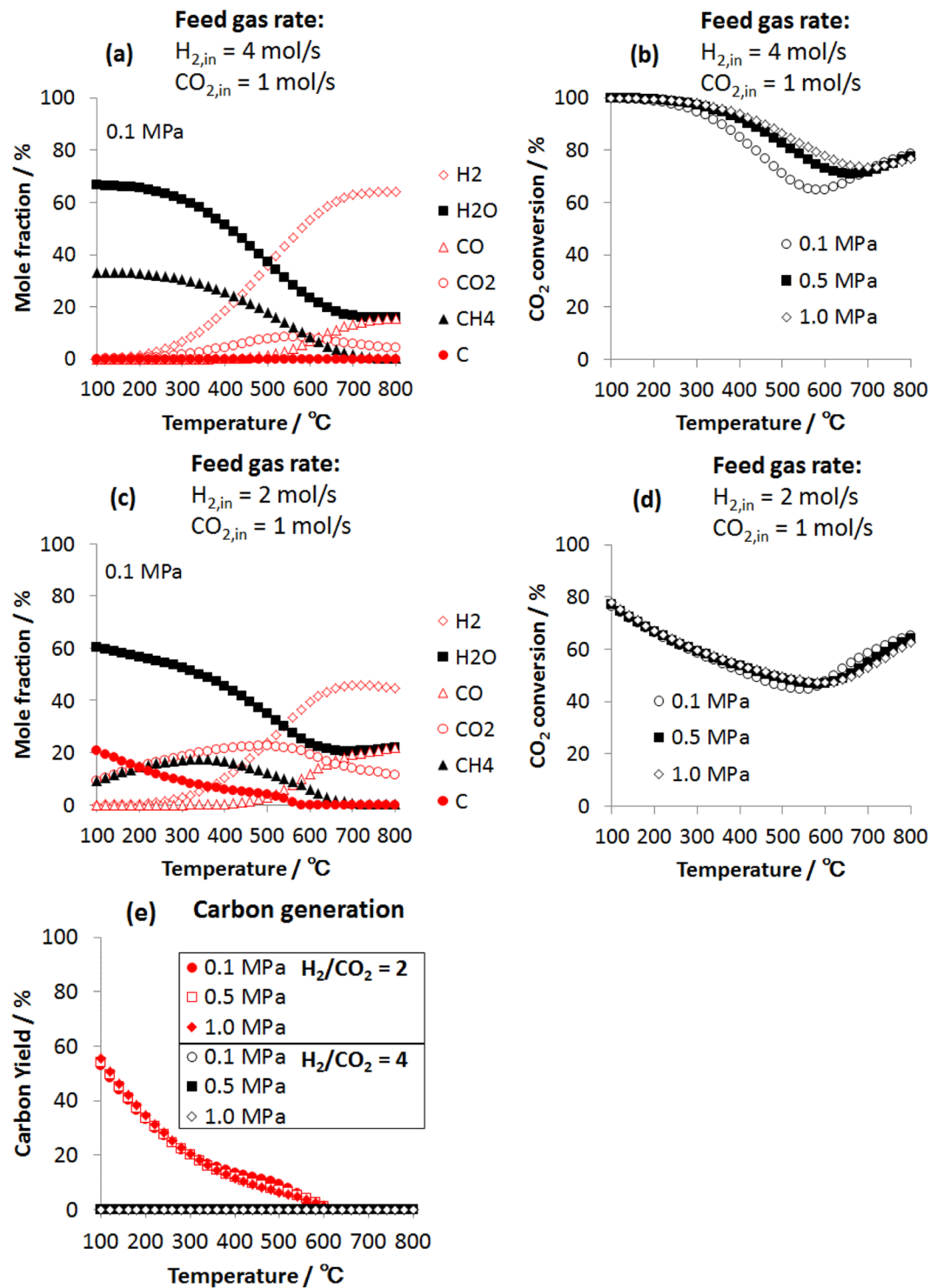


Figure 2. Equilibrium composition of the CO₂ hydrogenation products as a function of temperature computed following the Gibbs energy minimization method. **(a)** Molar fraction of possible products for a feed gas ratio H₂/CO₂ of 4. **(b)** CO₂ conversion for a feed gas ratio H₂/CO₂ of 4. **(c)** Molar fraction of possible products for a feed gas ratio H₂/CO₂ of 2. **(d)** CO₂ conversion for a feed gas ratio H₂/CO₂ of 2. **(e)** Effect of the feed gas ratio H₂/CO₂ on the carbon generation process.

conditions that can have an impact on the system running costs. As mentioned above, maintaining a feed gas rate H₂/CO₂ of 4 avoids the generation of solid carbon. The generation of solid carbon affects the catalyst activity and decreases its lifetime, which directly impact the running cost of the system. Another factor that can impact the system running costs is high temperatures. Catalyst sintering is favored at high temperatures and this causes a

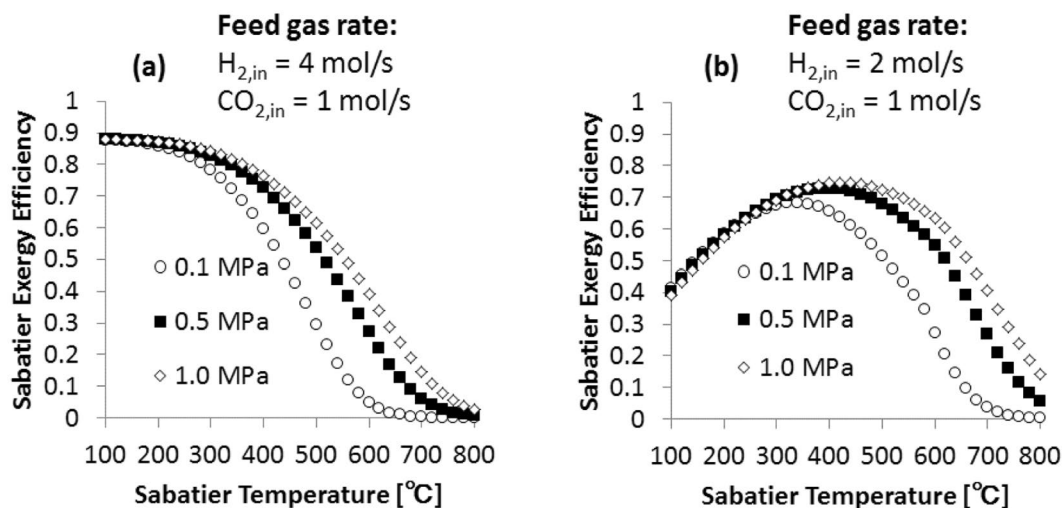


Figure 3. Exergy efficiency of the Sabatier process as a function of temperature for H_2/CO_2 of 4 (a) and 2 (b).

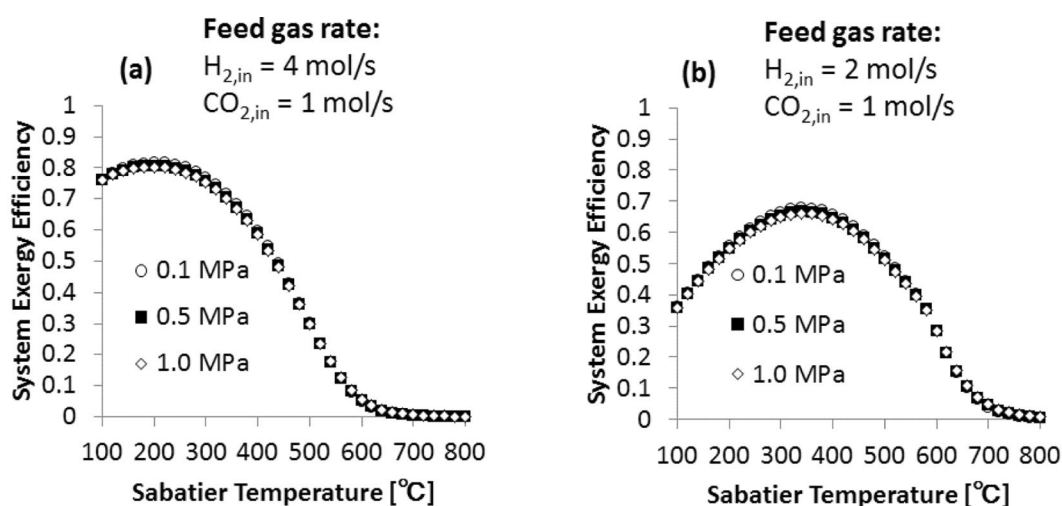


Figure 4. Overall exergy efficiency of the water electrolyzer and CO_2 hydrogenation tandem system as a function of temperature for H_2/CO_2 of 4 (a) and 2 (b).

loss in the catalyst activity^{12,18–21}. So that, by operating the system at a relative low temperature (100–300°C) helps to avoid catalyst sintering.

In summary, our thermodynamic analysis of the water electrolyzer- CO_2 hydrogenation tandem system exposes the conditions at which high exergy efficiency can be achieved. The results also show that the thermal coupling within the CO_2 hydrogenation and water electrolysis processes contributes to increase the overall exergy efficiency of the system.

Methods

In the analysis a steady state and steady flow are assumed. Chemical kinetics effects are not considered in the calculations. All values of enthalpy, Gibbs free energy and entropy for all the species were computed using Aspen Plus V8.8, Aspen TechTM.

Water electrolysis. The theoretical energy required to split liquid H_2O into gaseous H_2 and O_2 is equal to the enthalpy change (ΔH_{elec}) of H_2O , which is a function of temperature and pressure and can be calculated with the following equation:

$$\Delta H_{elec} = \Delta G_{elec} + T\Delta S_{elec} \quad (8)$$

where ΔG is the Gibbs free energy change and ΔS is the entropy change. These thermodynamic parameters are a function of the operative temperature (T) and pressure (P). The theoretical energy ΔH corresponds to the sum of electrical energy demand ΔG and thermal energy demand $T\Delta S$ (Q_{demand}). ΔH , ΔG and ΔS were calculated using the following equations:



$$\Delta H = (h_{\text{H}_2(g)}(T, P) + h_{\text{O}_2(g)}(T, P)) - (h_{\text{H}_2\text{O}(l)}(T, P)) \quad (10)$$

$$\Delta G = (g_{\text{H}_2(g)}(T, P) + g_{\text{O}_2(g)}(T, P)) - (g_{\text{H}_2\text{O}(l)}(T, P)) \quad (11)$$

$$\Delta S = (s_{\text{H}_2(g)}(T, P) + s_{\text{O}_2(g)}(T, P)) - (s_{\text{H}_2\text{O}(l)}(T, P)) \quad (12)$$

Where $h_{\text{H}_2(g)}$, $h_{\text{O}_2(g)}$ and $h_{\text{H}_2\text{O}(l)}$ are respectively the enthalpy values of H_2 and O_2 in gaseous phase, and H_2O in liquid phase. $g_{\text{H}_2(g)}$, $g_{\text{O}_2(g)}$ and $g_{\text{H}_2\text{O}(l)}$ are respectively the Gibbs free energy of H_2 and O_2 in gaseous phase, and H_2O in liquid phase. $s_{\text{H}_2(g)}$, $s_{\text{O}_2(g)}$ and $s_{\text{H}_2\text{O}(l)}$ are respectively the entropy of H_2 and O_2 in gaseous phase, and H_2O in liquid phase. The enthalpy, Gibbs free energy and entropy values were computed using Aspen Plus V8.8, Aspen Tech™.

The exergy input for a water electrolysis process corresponds to the electrical energy demand, which is the minimum work required to split H_2O into H_2 and O_2 . Then, the exergy input is:

$$Ex_{in} = \Delta G_{elec} = \Delta H_{elec} - Q_{demand} \quad (13)$$

CO₂ hydrogenation process. The equilibrium composition of the reactions was calculated using the Gibbs free energy minimization method, which is a widely used method to perform thermodynamic analysis of reacting systems^{20,21,25}. The equilibrium composition and the enthalpy of reaction (ΔH_r) for the CO₂ hydrogenation possible products were computed using Aspen Plus V8.8, Aspen Tech™. The species considered in the analysis are: CH₄, CO, CO₂, H₂O, H₂ and C (solid carbon). All the species were considered in gas phase, with the exception of C, which was considered in solid phase. The computations were carried out in the temperature range of 100 °C–800 °C and at different pressures.

The thermodynamic conversion of CO₂, CH₄ generation and carbon generation were calculated from the equilibrium composition results using the following equations:

$$\text{CO}_2 \text{ conversion } [\%] = \frac{\text{CO}_{2,in} - \text{CO}_{2,out}}{\text{CO}_{2,in}} \times (100) \quad (14)$$

$$\text{CH}_4 \text{ generation } [\%] = \frac{\text{CH}_{4,out}}{\text{CO}_{2,in}} \times (100) \quad (15)$$

$$\text{Carbon generation } [\%] = \frac{C_{out}}{\text{CO}_{2,in}} \times (100) \quad (16)$$

Where $\text{CO}_{2,in}$ and $\text{CO}_{2,out}$ are the molar flow rate of CO₂ at inlet and outlet, respectively. $\text{CH}_{4,out}$ is the molar flow rate of CH₄ at outlet. C_{out} is the molar flow rate of solid carbon at outlet.

Exergy calculation. The exergy coming out (Ex_{out}) of the system is calculated based on the CH₄ generation molar rate:

$$Ex_{out} = \text{CH}_{4,out} \cdot (Ex_{\text{CH}_4}) \quad (17)$$

The exergy of a specific gas (Ex_i) is equal to the sum of physical exergy (Ex_i^{Ph}) and chemical exergy (Ex_i^{Ch}):

$$Ex_i = Ex_i^{Ph} + Ex_i^{Ch} \quad (18)$$

The physical exergy is calculated according the following equation:

$$Ex_i^{Ph} = m_i[(h_i - h_0) - T_0(S_i - S_0)] \quad (19)$$

where m_i is the molar flow rate of the gas, h_i is the enthalpy of the gas at the Sabatier reaction conditions, and h_0 is the enthalpy at the gas at the dead state. T_0 is the temperature at the dead state. S_i is the entropy of the gas at the Sabatier conditions and S_0 is the gas entropy at the dead state. The dead state conditions are assumed to be 298.15 K and 1 atm. The chemical exergy is calculated using the following equation:

$$Ex_i^{Ch} = m_i \cdot (Ex_{0,i}) \quad (20)$$

where $Ex_{0,i}$ is the standard chemical exergy of the gas.

For the heat flow from the Sabatier reactor (Q_{sab}) to the water electrolysis system, the exergy is calculated as follows:

$$Ex_{heat} = Q_{demand} \left(1 - \frac{T_{elec}}{T_{sab}} \right) \quad (21)$$

where $Q_{Sab} \geq Q_{demand}$, otherwise, there is not heat transfer. T_{elec} and T_{sab} are the temperatures of the electrolysis system and Sabatier reactor, respectively.

Calculation of the overall exergy efficiency of the water electrolyzer and CO₂ hydrogenation tandem system:

$$\eta_{overall}^{ex} = \frac{CH_{4,out} \cdot (Ex_{CH_4})}{\Delta H_{elec} - Q_{demand} \left(1 - \frac{T_{elec}}{T_{sab}} \right)} \quad (22)$$

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Author Contributions

Y.S., H.M. and T.A. designed the concept. Y.M. and O.S.M.-H. assisted with the design of the concept and carried out the calculations. A.S. and M.I. discussed the calculation results. All authors discussed the results and commented on the manuscript.

Additional Information

Competing Interests: The authors declare no competing interests.

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